



(12) Ausschließungspatent

(11) DD 301 708 A5

Erteilt gemäß § 17 Absatz 1  
Patentgesetz der DDR  
vom 27. 10. 1983

5(51) A 01 N 55/02  
A 01 N 37/44

in Übereinstimmung mit den entsprechenden  
Festlegungen im Einigungsvertrag

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DEUTSCHES PATENTAMT

In der vom Anmelder eingereichten Fassung veröffentlicht

(21) DD A 01 N / 313 605 7

(22) 04. 12. 87

(44) 22. 07. 93

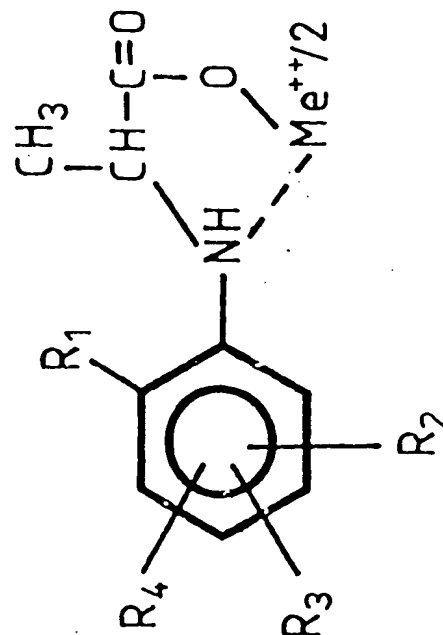
(47) 07. 05. 92

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(54) Mittel mit fungizider Wirkung

(55) Fungizides Mittel; Phytophthora infestans;  
N-Phenylalanin-Kupferkomplex; substituierte  
N-Phenylalanin-Metallkomplexe; phytopathogene Pilze;  
Kartoffel; Tomate

(57) Die Erfindung betrifft ein Mittel mit fungizider Wirkung zur Bekämpfung von Pilzkrankheiten in landwirtschaftlichen, gärtnerischen und forstwirtschaftlichen Kulturpflanzenbeständen. Erfindungsgemäß enthalten sie neben den bekannten Hilfs- und Trägerstoffen als neuen Wirkstoff Kupferkomplexe substituierten N-Phenylalanins der allgemeinen Formel, worin R<sub>1</sub> einen Alkyl- oder Alkoxyrest von 1 bis 4 C-Atomen oder Halogen, R<sub>2</sub> und R<sub>3</sub> jeweils ein H-Atom oder Alkylreste mit 1 bis 3 C-Atomen, Alkoxyreste von 1 bis 4 C-Atomen oder Halogen, R<sub>4</sub> ein H-Atom oder Methylrest, Me ein zwei- oder dreiwertiges Metallion, vorzugsweise Cu<sup>++</sup>, Zn<sup>++</sup>, Mn<sup>++</sup>, Co<sup>++</sup>, Ni<sup>++</sup>, Fe<sup>++</sup>/Fe<sup>+++</sup> bedeuten, Formel



Die Anwendung der erfindungsgemäßen Mittel erfolgt in den für Fungizide üblichen Zubereitungs- bzw. Ausbreitungsformen, wie Lösungen, Emulsionen, Suspensionen und Konzentrationen als Spritz- oder Stäubemittel. Diese Formulierungen werden in der üblichen Art und Weise unter Zusatz von Formulierungshilfsstoffen, wie Lösungsmitteln, Trägerstoffen, Emulgier- und Dispergiermitteln, Haftmitteln, hergestellt.

Die erfindungsgemäßen Mittel entsprechend der allgemeinen Formel können gegebenenfalls gemeinsam mit anderen Agrochemikalien, wie z. B. Pflanzenschutz- und Schädlingsbekämpfungsmitteln, Mitteln zur Steuerung biologischer Prozesse oder Bodenverbesserungsmitteln, aber auch mit anderen agrotechnischen Maßnahmen appliziert worden, wobei vorzugsweise Aufwandmengen von 0,1 bis 3,0 kg Wirkstoff/ha eine erfindungsgerechte Wirkung garantieren.

Die nachfolgenden Beispiele dienen der Erläuterung der Erfindung, ohne sie einzuschränken.

### Ausführungsbeispiele

#### Beispiel 1

Wirkung gegen *Phytophthora infestans* auf Tomaten (*Solanum lycopersicum*)

Fiederblätter von Tomatenpflanzen im 10- bis 12-Blatt-Stadium der Sorte „Harzfeuer“ wurden in die Fungizidbrühe (25 Fiederblätter/Variante) getaucht. Nach dem Abtrocknen des Fungizidbelages (etwa 3 Stunden nach dem Tauchen) wurden die Blätter mit einer Zoosporen-/Sporangiensuspension von *Phytophthora infestans* (Pathotyp 1.2.3.4.5.7.10.11.) durch Aufsetzen von 10 Tropfen der Erregersuspension infiziert. Die Blätter lagerten 5 bis 6 Tage bei 90 % bis 95 % rel. Luftfeuchte und 10°C bis 20°C. Für die Verwertung der fungiziden Wirkung wurde die Anzahl der angangenen Infektionen ausgezählt und die Infektionsrate (IR %) bzw. der Wirkungsgrad (WG %) errechnet.

Die mit der erfindungsgemäßen Verbindung nach der Formel I ermittelten Wirkungsgrade bei Konzentrationen zwischen 50 und 200 µg/ml sind im Vergleich zu bekannten Standardfungiziden in Tabelle 1 zusammengefaßt.

Tabelle 1

Wirkung der erfindungsgemäßen Verbindung nach Formel I bei verschiedenen Aufwandmengen gegen die Krautfäule der Kartoffel und Tomate ( $\bar{x}$  aus 3 Versuchen)

Variante	µg/ml	Wirkungsgrad %
1 bercema-Zineb 90	200	32,6
2 bercema-Ridomil/Zineb	13,5/109	76,3
3 Verbindung nach Formel I	200	79,3
4 Verbindung nach Formel I	150	62,5
5 Verbindung nach Formel I	100	37,9
6 Verbindung nach Formel I	50	4,5

Infektionsrate  $\bar{x}$  99,1. Applikation durch Tauchen in die Mittelbrühe. Inokulation mit *P. infestans* 3 Stunden nach Applikation.

#### Beispiel 2

Protektive Wirkung der erfindungsgemäßen Verbindung nach Formel I bei Metalaxyl-resistenten und -sensiblen Stämmen von *Phytophthora infestans* ( $\bar{x}$  von 3 Versuchen)

Variante	µg/ml	Wirkungsgrad %	
		Metalaxyl-resistent	Metalaxyl-sensibel
1 bercema-Zineb 90	200	21,9	67,4
2 bercema-Ridomil/Zineb	13,5/109	11,1	78,0
3 Verbindung nach Formel I	200	88,0	94,3
	(50 % WP)		
	100	88,0	76,3

$\bar{x}$  IR % Isolat mit Resistenz 100%

$\bar{x}$  IR % Isolat ohne Resistenz 98%

Formel I

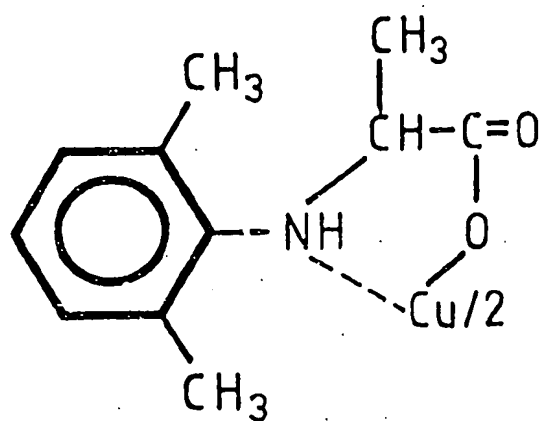


TABLE I

 $\Delta\nu_M$  VALUES (CPS) AT VARIOUS TEMPERATURES FOR Co(II) AND Ni(II)

	Temp., °C						
	50	55	60	65	70	75	80
$\Delta\nu_M(\text{Co(II)})$	384	348	313	307	272	245	211
$\Delta\nu_M(\text{Ni(II)})$	...	...	...	1310	1270	1240	1210

TABLE II

SUMMARY AND COMPARISON OF RESULTS

Ion	$10^{-4}M$ , cps	$\Delta H^\ddagger$ , kcal/mole	$\Delta S^\ddagger$ , eu	$10^{-4}k$ , sec $^{-1}$	Ref
Ni(II)	$-5.21 \pm 0.41$	$11.8 \pm 0.8$	$-0.2 \pm 2.5$	1.24	This work
Ni(II)	-2.03	10.0	-8.8	0.30	6
Ni(II)	$-8.1 \pm 0.5$	$11.7 \pm 0.1$	$-3.6 \pm 1.0$	0.24	7
Co(II)	$-1.85 \pm 0.10$	$8.4 \pm 0.6$	$-7 \pm 2$	15	This work
Co(II)	-0.228	$8.1 \pm 0.5$	$-7.5 \pm 2$	15	6

The reasons for the differences, especially between the nickel(II) perchlorate salts, are not known.

It is well known that  $\sigma$  and  $\pi$  electrons of a central metal ion in a complex may affect resonance signals of ligand nuclei in different ways. This is true because  $\sigma$  and  $\pi$  metal orbitals interact with ligand orbitals of their own symmetry. A consideration of electron delocalization and spin polarization in metal-acetonitrile complexes leads one to expect that  $\sigma$  electrons in metal  $e_g$  orbitals will cause an upfield shift and that  $\pi$  electrons in metal  $t_{2g}$  orbitals will cause a downfield shift of the metal proton signal. The observed shifts are in agreement with this expectation. Thus the upfield shift in the Ni(II) solutions is due to the two unpaired  $e_g$  electrons, whereas the smaller upfield shift in the Co(II) solutions is the net result of an upfield shift from the two unpaired  $e_g$  electrons and a downfield shift from the unpaired  $t_{2g}$  electron.

The Co(II) rate constants were evaluated using eq 10b of Swift and Connick.<sup>10</sup> The activation parameters were evaluated from a least-squares treatment of the equation

$$\log \frac{6}{\tau_M} - \log T' = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT} \quad (2)$$

where  $6/\tau_M$  is the rate constant for the exchange of a solvent molecule of the hexacoordinated complex, and the other symbols have their usual meanings. For Co(II) the enthalpy of activation was found to be  $8.4 \pm 0.6$  kcal mole $^{-1}$  and the entropy of activation was  $-7 \pm 2$  cal deg $^{-1}$  mole $^{-1}$ . The data for a  $1.72 \times 10^{-2} M$  solution of Co(II) are given in Table III. Data from three other concentrations gave identical results.

The Ni(II) rate constants were evaluated in the temperature range from 65 to 80° using eq 10b of Swift and Connick.<sup>10</sup> Use of this equation involves the assumption that  $(1/\tau_M)^2 \gg \Delta\nu_M^2$ . At 65° this assumption introduces an error smaller than 3%. At the temperatures 60 and 55° the rate constants were determined using the equation

$$\frac{1}{T_{2p}} = \frac{P_{M\tau_M}\Delta\nu_M^2}{1 + \tau_M^2\Delta\nu_M^2} \quad (3)$$

TABLE III

DATA FOR  $\text{Co}(\text{CH}_3\text{CN})^{2+}$ -SOLVENT EXCHANGE FOR  $1.72 \times 10^{-2} M \text{ Co(II)}$ 

$10^4/T$	$\Delta\nu_M$ , cps	$\Delta\nu_M$ , cps	$\log (6/\tau_M)$
3.55	0.25	643	4.757
3.60	0.28	673	4.738
3.66	0.45	712	4.572
3.72	0.58	744	4.502
3.77	0.85	777	4.396
3.88	1.62	837	4.155
3.97	2.18	891	4.084

and obtaining  $\Delta\nu_M$  values from extrapolation of the least-squares treatment of  $\Delta\nu_M$  vs.  $1/T$  to the desired temperatures. The activation parameters were evaluated by a least-squares treatment of eq 2 using the Ni(II) data. The values obtained were  $\Delta H^\ddagger = 11.8 \pm 0.8$  kcal mole $^{-1}$  and  $\Delta S^\ddagger = -0.2 \pm 2.8$  cal mole $^{-1}$  deg $^{-1}$ .

The rate constants and activation enthalpies and entropies are listed in Table II together with those previously obtained.<sup>6,7</sup> The reported activation enthalpies for both ions are in agreement within experimental error; the  $\Delta H^\ddagger$  values reported here and by Ravage, Stengle, and Langford for Ni(II) are in especially good agreement, as are those reported here and by Matwiyoff and Hooker for Co(II). The agreement indicates that the Co(II) and Ni(II) cations are most likely not complexed by the anions of the two different salts and that the assumption of complete dissociation of these salts in acetonitrile is probably justified. If the perchlorate and tetrafluoroborate salts are completely ionized, the differences noted for the reported coupling constants cannot be explained on the basis of partial complexing of the cations by one or both of the anions.

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## Dimeric Copper(II) Levulinate Hydrate

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Received May 22, 1967

Copper(II) alkanoates form an interesting class of compounds, whose magnetic susceptibility at room temperature is lower than that required for one unpaired spin.<sup>1</sup> The molecular structure of cupric acetate,<sup>2</sup> cupric succinate,<sup>3</sup> cupric acetate monopyridine,<sup>4</sup> and similar compounds, as determined by X-ray diffraction, consists of a dimeric unit with four carboxylate groups bridging the two copper atoms. The close approach of the two metal atoms in the dimer (2.64 Å) implies the

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existence of an interaction between the two units of the dimer, and this is responsible for the low magnetic moment. The nature of this interaction has been treated by valence bond<sup>5</sup> and molecular orbital<sup>6</sup> methods and neither approach could explain successfully all of the properties. Recently, Hansen and Ballhausen<sup>7</sup> considered the interaction between the two units of the dimer by a coupled chromophore model, which assumes no direct bonding between the two units.

Although a wide variety of copper(II) salts with carboxylic acids have been investigated,<sup>1</sup> compounds of ketocarboxylic acids are not known. In this note, the preparation and characterization of dimeric copper(II) levulinate hydrate are reported.

### Experimental Section

**Preparation of the Compound.**—To about 2 g of levulinic acid,  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$  (obtained through the courtesy of Crown Zellerbach Co., Canas, Wash.), dissolved in 50 ml of water, finely divided copper carbonate (BDH) was added in small lots. The suspension was warmed to  $\sim 60^\circ$  when vigorous reaction occurred with the evolution of  $\text{CO}_2$ . The addition of the metal carbonate was continued until there was no reaction. The solution was filtered and the filtrate concentrated when dry air was passed over it; bluish green crystals of the complex were obtained in about 2 days. The crystals were separated from the mother liquor, washed with small amounts of acetone, and dried over fused  $\text{CaCl}_2$  *in vacuo*.

**Analysis.**—Copper in the compound was estimated gravimetrically as  $\text{Cu}(\text{py})_2(\text{NCS})_2$  and carbon by the semimicro combustion method. *Anal.* Calcd for  $\text{Cu}(\text{OOCCH}_2\text{CH}_2\text{COCH}_3)_2 \cdot \text{H}_2\text{O}$ : Cu, 20.40; C, 38.52. Found: Cu, 20.58; C, 39.10.

**Properties.**—The compound is a blue-green crystalline solid, freely soluble in water but sparingly soluble in acetone, methanol, and dioxane. It is insoluble in benzene. The solutions of the compound in organic solvents are intense greenish blue, whereas its aqueous solution is pale blue.

**Apparatus and Procedure for Physicochemical Studies.**—The magnetic susceptibility of the complex was determined at room temperature by the Gouy method, using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. The reflectance spectrum of the powdered sample was obtained with a standard reflectance attachment to the Hilger Uvispek spectrophotometer, Model H 700, using magnesium oxide as the reference material. The solution spectra of the compound in acetone and water were obtained with the same instrument using a pair of 1-cm matched quartz cells. The concentrations used for the solution spectra are 0.005–0.007 *M* in acetone and 0.02 *M* in water. The infrared spectrum of the solid was recorded in a KBr pellet with a Carl Zeiss UR 10 spectrophotometer. The electrical conductivity measurements of the complex in 1,4-dioxane and in water were carried out with a Siemen's conductivity bridge, employing platinized Pt electrodes (cell constant = 0.600). The molecular weight of the compound in pure dry 1,4-dioxane and in water was determined by the cryoscopic method ( $K_f$  for dioxane =  $5.00^\circ$ ).

### Results and Discussion

The molar magnetic susceptibility of the compound at  $27^\circ$  is  $832 \times 10^{-6}$  cgs, emu. The correction for the diamagnetism for the two levulinate groups and the water molecule is  $136 \times 10^{-6}$  cgs, emu. The corrected

molar magnetic susceptibility,  $\chi_M$ , is therefore  $968 \times 10^{-6}$  cgs, emu. The effective magnetic moment per copper, calculated using the formula  $2.839[(\chi_M - 60 \times 10^{-6})7]^{1/2}$ , is 1.48 BM. The reflectance spectrum of the solid shows absorption maxima at 375 and 680  $m\mu$ . The 375- $m\mu$  band is considered to be characteristic of the dimeric molecule.<sup>8</sup> The presence of this band in copper(II) levulinate monohydrate and the low magnetic moment suggest a dimeric structure similar to that of copper(II) acetate.<sup>9</sup> The other band at 680  $m\mu$  is the usual "copper band."

The electronic spectrum of the compound in acetone shows absorption maxima at 370 ( $\epsilon \approx 60$ ) and 680  $m\mu$  ( $\epsilon \approx 150$ ). This implies that the dimeric structure persists in this solvent. The comparatively high intensity of the 680- $m\mu$  band is probably due to the acentric site symmetry of the copper atom in the dimeric unit. The point group of half of the dimer would be  $C_{4v}$  around the copper atom. In water, the compound shows a broad absorption band around 800  $m\mu$  with low intensity ( $\epsilon \approx 25$ ). The position and the low intensity of the band together with the absence of the 375- $m\mu$  band suggest that only a monomeric centrosymmetric copper(II) species is present in aqueous solution.

The conductivity and the molecular weight determinations of the compound in 1,4-dioxane and in water also support the foregoing conclusions. The solutions of the compound in dioxane ( $10^{-3}$  to  $10^{-6}$  *M*) are nonconducting, the resistance being around  $10^6$  ohms. In aqueous solution ( $2.5 \times 10^{-3}$  *M*), the molar conductance of the compound is  $120 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ . The molecular weight of the compound in dioxane is almost twice its monomeric formula weight when the concentration is 0.067 *M* (Table I), whereas in water the values indicate dissociation of the monomer, forming ionic species.

TABLE I  
MOLECULAR WEIGHT DETERMINATION OF COPPER(II)  
LEVULINATE MONOHYDRATE IN WATER AND 1,4-DIOXANE\*

In water			In dioxane		
Concn in moles/1000 g of solvent	<i>M</i>	$n^* = M/M_0$	Concn in moles/1000 g of solvent	<i>M</i>	$n^* = M/M_0$
0.02560	99	0.320	0.00729	450	1.45
0.03380	130	0.417	0.02662	495	1.60
0.05133	139	0.447	0.04900	545	1.70
0.06753	149	0.479	0.06700	600	1.93

\* Formula weight of the monomer,  $M_0 = 311.54$ .  $n^*$  denotes the molecular complexity in solution.

The infrared spectral frequencies of the complex and sodium levulinate together with their probable assignments are given in Table II. Levulinic acid contains a  $\gamma$ -keto function. Both the acid<sup>10</sup> and its sodium salt show a strong infrared absorption at  $\sim 1725 \text{ cm}^{-1}$ , which is assigned to the carbonyl stretch of the  $\gamma$ -keto

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group. The presence of this band in the copper(II) compound at  $1724\text{ cm}^{-1}$  reveals that the keto group is not involved in bonding to the metal. A sharp strong band at  $1600\text{ cm}^{-1}$  in the copper(II) complex is due to the antisymmetric COO stretching vibration. In the copper(II) alkanoates where there is a dimeric (or polymeric) structure involving a bridging of two copper atoms by four carboxylate groups, the antisymmetric COO stretching mode occurs as a sharp band at  $1600\text{ cm}^{-1}$ , while in the monomeric copper(II) alkanoates, only a broad band in the region  $1560\text{--}1600\text{ cm}^{-1}$  is observed.<sup>11,12</sup> The presence of a sharp band at  $1600\text{ cm}^{-1}$  in copper(II) levulinate supports the dimeric structure of the compound. The  $\text{CH}_2$  rocking vibration, which is considered to be very sensitive to any deformations in the organic molecular chain,<sup>9</sup> occurs around  $770\text{ cm}^{-1}$  both in the sodium salt and in the copper(II) compound. This suggests that the levulinate ion does not undergo any structural deformation on complex formation.

TABLE II  
INFRARED SPECTRAL FREQUENCIES OF LEVULINATES  
IN KBr PELLET AND THEIR ASSIGNMENT

Sodium levulinate n-hydrate	Copper(II) levulinate monohydrate	Probable assignment
1724 vs	1724 vs	C=O str
1560 vs	1600 vs	Antisym COO str +
1580		H <sub>2</sub> O bend
1455 vs	1450 vs	Symmetric COO str
1420 vs	1420 s	CH <sub>2</sub> bend
1375 s	1378 s	CH <sub>2</sub> twist and wag
1280 m	1320 m	
1255 m	1240 m	
1175 s	1175 s	
1060 m	1068 w	
988 w	1030 w	CC str
938 w	995 w	
925 m	950 w	
825 m	830 w	H <sub>2</sub> O rock
765 m	770 m	CH <sub>2</sub> rock
	760 w	...
	725 w	...
700	685 m	COO def

**Acknowledgment.**—The authors thank Professor M. R. A. Rao for his keen interest in this work.

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## Octacarbonyldiiododiiron(I): Preparation and Properties<sup>1</sup>

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Received May 29, 1967

The structure of dimanganese decacarbonyl is well established<sup>2</sup> as dinuclear with two square-pyramidal

$\text{Mn}(\text{CO})_5$  units joined solely by a manganese-manganese bond to give a staggered structure with  $D_{4d}$  symmetry. In this way, each valence shell orbital of each manganese atom participates in the formation of a doubly occupied bonding molecular orbital or else constitutes a filled, more or less nonbonding orbital. The effective utilization of all valence shell orbitals of the metal atoms which this structure permits affords a satisfactory basis for explaining the stability and diamagnetism of the molecule.

The ions  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$  and  $[\text{Co}_2(\text{CNCH}_3)_{10}]^{4+}$  are isoelectronic with  $\text{Mn}_2(\text{CO})_{10}$  and are known to have similar structures. In the case of  $[\text{Co}_2(\text{CNCH}_3)_{10}]^{4+}$  this structural similarity has been proved conclusively by a single-crystal X-ray study<sup>3</sup> while for  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$  the infrared spectrum suggests that this is the case.<sup>4</sup> Finally, the compound  $\text{Mn}_2(\text{CO})_8(\text{P}(\text{C}_2\text{H}_5)_3)_2$  has been shown<sup>5</sup> by X-ray methods to have a structure derived from that of  $\text{Mn}_2(\text{CO})_{10}$  by replacing the two axial CO groups by the phosphines. In all cases  $D_{4d}$  symmetry is proved or reliably indicated by the evidence at hand. Observations such as these, suggesting the stability of such a structure over a wide range of charges and metal atomic numbers, led us to consider the possibility of preparing an isoelectronic and isostructural compound of iron.

### Results

**Preparation and Properties of Diiododiiron Octacarbonyl.**—The new compound,  $\text{Fe}_2(\text{CO})_8\text{I}_2$ , has been prepared by the reaction of iodine with triiron dodecacarbonyl. It is a white crystalline solid, melting at ca.  $-5^\circ$  to a red liquid and it dissolves in a variety of organic solvents to give pale red solutions. Solutions in alkanes or ethers are moderately stable but solutions in chlorinated solvents such as chloroform decompose rapidly. The compound is air sensitive and must be stored under oxygen-free nitrogen or under vacuum. The compound in solution appears, from the observation of proton spectra of the solvents, to be diamagnetic. No esr signal was detected in any solution.

The infrared spectrum (see Table I and Figure 1a and b) of the compound, in pentane or THF solution, throughout the range  $750\text{--}3600\text{ cm}^{-1}$ , consists of only two strong bands, of nearly equal intensities, at  $1980$  and  $2000\text{ cm}^{-1}$ . This strongly suggests that the structure of the molecule is as shown in Figure 2. This structure had  $D_{4d}$  symmetry, and, applying the usual symmetry analysis, it is found that just two infrared-active CO stretching modes, corresponding to the representations  $e_1$  and  $b_2$ , are expected. Of course, the rotationally eclipsed structure, with symmetry  $D_{4h}$ , would also have just two infrared-active CO stretching frequencies and is thus equally compatible with the

(1) (a) Supported, in part, by a grant from the National Science Foundation; (b) a brief preliminary report of this work has been presented earlier: F. A. Cotton, T. G. Dunne, B. F. G. Johnson, and J. S. Wood, *Proc. Chem. Soc.*, 176 (1964).

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